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EUROPEAN PATENT APPLICATION

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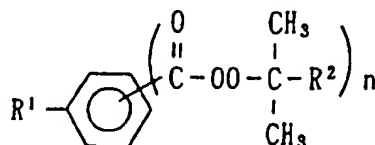
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(54) Vulcanizable rubber composition.

(57) A vulcanizable rubber composition which contains an iodine- or bromine-containing rubber and an organic peroxide of the formula:



(I)

wherein R¹ is a hydrogen atom, a chlorine atom or methyl group, R² is a linear or branched alkyl group having 2 to 5 carbon atoms, and n is an integer of 1 to 3, generates only a small amount of methyl iodide or methyl bromide during the vulcanization.

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method using rolls for rubber, a pressurizing kneader and the like. The composition according to the present invention can be vulcanized under conditions which are used for vulcanizing a usual rubber. For example, the rubber composition is mixed by rolls, the composition is injected in a mold; a press vulcanization is conducted at 100 to 200°C and 20 to 100 kg/cm²G for 5 to 180 minutes, and then an oven vulcanization is optionally conducted in an oven at 150 to 300°C for 10 to 240 minutes to prepare a vulcanized rubber.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be illustrated by the following Examples which do not limit the present invention.

Examples 1

An iodine-containing rubber [Dai-el G-902 (vinylidene fluoride/hexafluoropropylene/tetrafluoroethylene terpolymer manufactured by Daikin Industries, Ltd.)] (100 parts by weight), MT-carbon black (MT-C) (20 parts by weight), triallyl isocyanurate (TAIC) (4 parts by weight) and t-hexyl peroxybenzoate (1.5 parts by weight) as an organic peroxide were homogeneously mixed by rubber rolls to prepare a vulcanizable composition.

Vulcanizability of the composition was evaluated by a curastometer at 150°C and 160°C. A lowest viscosity (M_L), a highest viscosity (M_H), an induction time (T_{10}) and an optimal vulcanization time (T_{90}) were measured. The composition was press vulcanized at 150°C for 10 minutes and then oven vulcanized at 180°C for four hours to prepare a sample of 1 mm thickness.

At ordinary state and after aging at 230°C for 70 hours, a 100 % tensile stress (M_{100}), a tensile strength at break (T_B), an elongation at break (E_B) and a hardness (Hs) were measured.

A compression set (C.S.) was measured for a sample of 13 mm thickness prepared by vulcanizing in the same conditions as in the above.

An amount of generated methyl iodide was measured when the composition was vulcanized at 160°C for 10 minutes. The amount of generated methyl iodide was measured by charging the vulcanizable composition in a closed vessel, vulcanizing the composition and then determining the amount of methyl iodide present in a vacant part of the vessel by means of a gas chromatography.

Results are shown in Table.

Example 2

The same procedure as in Example 1 was repeated except that the organic peroxide was used in an amount of 0.8 part by weight. Results are shown in Table.

Example 3

The same procedure as in Example 1 was repeated except that the organic peroxide was used in an amount of 0.4 part by weight. Results are shown in Table.

Comparative Example 1

The same procedure as in Example 1 was repeated except that 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane (Perhexa 2.5 B manufactured by Nippon Oil and Fats Co., Ltd.) (1.5 parts by weight) was used as the organic peroxide and the press vulcanization was conducted at 160°C for 10 minutes. Results are shown in Table.

Table

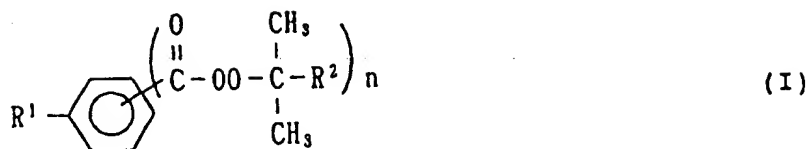
	Com. Ex. 1	Ex. 1	Ex. 2	Ex. 3
G-902	100	100	100	100
MT-C	20	20	20	20
TAIC	4	4	4	4
Peroxide 1*	1.5	—	—	—
† 2*	—	1.5	0.8	0.4
Vulcanizability (160°C)				
ML (kg·f)	0.12	0.23	0.24	0.18
MH (kg·f)	3.80	7.20	7.55	4.40
T10 (min.)	0.8	0.3	0.3	0.5
T90 (min.)	2.8	0.7	1.0	2.0
Vulcanizability (150°C)				
ML (kg·f)	—	0.24	0.22	0.21
MH (kg·f)	—	5.80	4.80	3.75
T10 (min.)	—	0.3	0.5	0.7
T90 (min.)	—	1.2	2.3	4.3
Vulcanizing condition				
Press vulcanization				
Temperature (°C)	160	150	150	150
Time (min.)	10	10	10	10
Oven vulcanization				
Temperature (°C)	180	180	180	180
Time (hr.)	4	4	4	4
Properties at ordinary state				
M ₁₀₀ (kg·f/cm ²)	92	100	100	69
T _B (kg·f/cm ²)	208	193	169	187
E _B (%)	160	160	160	210
HS (JIS A)	74	74	74	74
Compression set (%)				
(200°C x 72 hrs.)	21	20	25	40
Amount of generated methyl iodide				
(mg/kg-comp)	258	49	26	12
Aging resistance				
(230°C x 70 hrs.)				
ΔM ₁₀₀ (%)	-26	-19	-11	-3
ΔT _B (%)	-14	-10	-21	+11
ΔE _B (%)	+13	+13	+12	±0
ΔHS (point)	-1	-1	-2	-1

Note) Peroxide 1: 2,5-Dimethyl-2,5-di(t-butylperoxy)hexane

Peroxide 2: t-Hexyl peroxybenzoate

Claims

1. A vulcanizable rubber composition which comprises an iodine- or bromine-containing rubber and an organic peroxide of the formula:



wherein R¹ is a hydrogen atom, a chlorine atom or methyl group, R² is a linear or branched alkyl group having 2 to 5 carbon atoms, and n is an integer of 1 to 3.

2. The composition according to claim 1, wherein an amount of the organic peroxide is from 0.1 to 5 parts by weight per 100 parts by weight of the rubber.
3. The composition according to claim 1, wherein the organic peroxide is selected from the group consisting of t-amyl peroxybenzoate, t-hexyl peroxybenzoate, 1,1,3,3-tetramethylbutyl peroxybenzoate, t-amyl peroxy-m-methylbenzoate, t-hexyl peroxy-m-methylbenzoate, 1,1,3,3-tetramethylbutyl peroxy-m-methylbenzoate, t-hexyl peroxy-p-methylbenzoate, t-hexyl peroxy-o-methylbenzoate, t-hexyl peroxy-p-chlorobenzoate, bis(t-hexyl peroxy)phthalate, bis(t-amyl peroxy)isophthalate, bis(t-hexyl peroxy)-isophthalate, bis(t-hexyl peroxy)terephthalate and tris(t-hexyl peroxy)trimellitate.
4. The composition according to claim 1, wherein the rubber is an iodine- or bromine-containing fluororubber.



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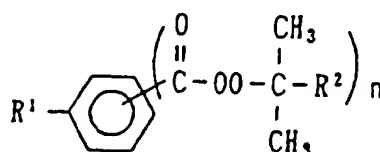
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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
Y	DE - A - 3 925 743 (NIPPON MEKTRON) * Page 2, lines 14-34, 52; page 3, line 41 - page 4, line 33; claims *	1-4
Y	EP - A - 0 410 351 (AUSIMONT S.r.l.) * Examples *	1-4
P, X	DE - A - 4 006 058 (LUPEROX) * Claims 3, 8, 15 *	1-4

CLASSIFICATION OF THE APPLICATION (Int. CL.5)
C 08 L 27/12 C 08 L 27/16 C 08 K 5/14 C 08 L 21/00

TECHNICAL FIELDS SEARCHED (Int. CL.5)
C 08 L 27/00 C 08 L 21/00 C 08 K 5/00

The present search report has been drawn up for all claims		
Place of search VIENNA	Date of completion of the search 13-10-1992	Examiner SEIRAFI

CATEGORY OF CITED DOCUMENTS
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document

Legend
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document

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